

AD-A129 307

SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY
LEVELS WITH SPECIAL..(U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY R W FIELD ET AL. 30 SEP 82

1//

UNCLASSIFIED

AFOSR-TR-83-0451 AFOSR-80-0254

F/G 7/4

NL

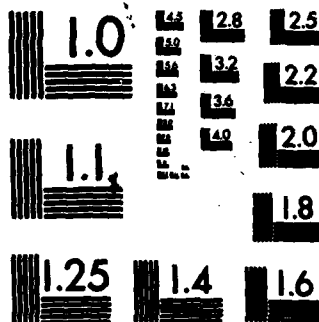


END

DATE

FORMED

DTIC



AFOSR-TR- 83 - 0451

(4)

AD A129307

FINAL REPORT

SEQUENTIAL EXCITATION PREPARATION OF MOLECULAR ENERGY
LEVELS WITH SPECIAL STRUCTURAL AND CHEMICAL PROPERTIES

AFOSR-80-0254

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139

Approved for public release;
distribution unlimited.

1 SEPTEMBER 1981 - 30 SEPTEMBER 1982

DTIC
ELECTE
JUN 13 1983
S
A

DTIC FILE COPY

88 06 10 073

Approved for public
release, distribution unlimited

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83-0451	2. GOVT ACCESSION NO. AD-A129307	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties		5. TYPE OF REPORT & PERIOD COVERED Final Report
7. AUTHOR(s) Robert W. Field James L. Kinsey		8. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		10. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0254
11. CONTROLLING OFFICE NAME AND ADDRESS AFOSR/NC Bolling Air Force Base Washington, D.C. 20332		12. REPORT DATE 30 Sep 82
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 6
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Stimulated Emission Pumping Modulated Gain Spectroscopy Formaldehyde <i>APPROX. 6000 cm⁻¹ then</i>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Three types of experiments are discussed: Stimulated Emission Pumping (SEP) on H₂CO, Modulated Gain Spectroscopy (MGS) on Na₂, and sub-Doppler spectroscopy of the Ca+O₂ flame. The SEP experiments have reached the intensive data-generation stage. With 10,000 cm⁻¹ of vibrational excitation, H₂CO is shown to behave as a normal mode oscillator in low rotational levels, exhibits extensive Coriolis mode mixing in J < 10, K_a < 4.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LP-014-6401

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

1000

rotational levels. A laser-locking scheme has improved the sensitivity of MGS by a factor of 10^3 . A new but puzzling assignment has been made of the $\text{Ca} + \text{O}_3$ flame orange band system.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

I. Research Progress

A. Pulsed Laser Experiments

Our Stimulated Emission Pumping and SEP-Stark experiments on the H_2CO molecule have started to yield huge quantities of spectral data. Nonrotating H_2CO , at vibrational energies up to $10,000\text{ cm}^{-1}$, appears to be behaving like a small molecule. The energies, rotational constants, and electric dipole moments of levels involving combinations of C-O stretch (ν_2) and out-of-plane bend (ν_4) seem to fit simple Dunham-type expansions. Two nearly degenerate pairs of vibrational levels have been located and the Fermi-interactions between them are so small ($<1\text{ cm}^{-1}$) that accidental mode-mixing at high energy seems likely to be a rare event. Coriolis- and c-axis interactions begin to appear at high J , K_a values.

These mode-mixing and K-mixing interactions are negligible when either J or K_a is small, but, by $J \approx 10$, $K_a \approx 4$, seem to couple all vibrational levels in the neighborhood of the 2_4 level accessible by SEP.

The most important results of our H_2CO SEP experiments are:

1. demonstration that non-rotating H_2CO is vibrationally well-organized. The normal-mode quantum numbers are good labels of the predominant vibrationally averaged structure. Near degenerate levels are capable of very different internal vibrational energy distributions (i.e. relative excitations of C-O vs. C-H stretch). This suggests that bond-specific chemistry might be observable in SEP-prepared H_2CO provided that the collisional cross-section for vibrational redistribution is smaller than that for chemical reaction.

2. suggestion that rotation, especially that about the C-O axis is an extremely effective mode-mixing mechanism. At high J , K_a , molecules forget their vibrational identity. All vibrational eigenstates begin to have similar internal vibrational energy distributions (because all nearly isoenergetic rotationless basis functions become intermixed by Coriolis interactions). Thus rotational heating will provide a severe limit to the observability and utility of bond-specific photochemistry.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
NOTICE OF TRANSMITTAL TO DTIC
This technical report has been reviewed and is
approved for public release IAW AFR 190-12.
Distribution is unlimited.
MATTHEW J. KERPER
Chief, Technical Information Division

I. Research Progress, Cont'd.

We plan to continue the H_2CO SEP experiments until we reach the maximum vibrational energy accessible by SEP. One particularly important spectroscopic question is whether the C-O stretch or out-of-plane bending vibration is more subject to Coriolis mixing with "background" levels. The two most important chemical questions that we hope to answer are: does tunnelling through the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ or $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ barrier become observable at SEP-accessible levels of the $\tilde{\chi}^1\text{A}_1$ state; are the total population removal rates from single vibration-rotation levels so large as to prohibit the observation of structure \leftrightarrow reactivity correlations. We also expect to initiate exploratory experiments on propynal, which is the smallest two-chromophore molecule known to have a bound excited electronic state and resolved rotational structure, the two prerequisites for SEP.

B. Modulated Gain Spectroscopy

Our Na_2 $\text{A}^1\Sigma_u^+ \rightarrow \text{X}^1\Sigma_g^+$ optically pumped laser is now excited by a cw dye laser and operating in a servo-controlled configuration that has resulted in a 10^3 -fold signal-to-noise improvement in modulated gain spectra. The sensitivity of the MGS scheme is now so great that we are observing many previously unobservable collisional and multiple resonance effects. The most interesting of these is laser oscillation from collisionally populated upper levels which appears only when the probe laser removes population from the lower level of the collisionally coupled transition.

Preliminary experiments with the new MGS scheme are nearly complete. We expect to resume systematically recording the spectra of the highest vibrational levels of the $\text{A}^1\Sigma_u^+$ and $\text{B}^1\Pi_u$ states of Na_2 .

C. Calcium Oxidation Reactions

The $\text{Ca} + \text{N}_2\text{O}$ and $\text{Ca} + \text{O}_3$ flames reactions result in completely dissimilar fluorescence excitation spectra in the 600nm region. There is not a single strong feature that appears in the spectra of both N_2O and O_3 flames. Our initial interpretation of the O_3 flames spectrum as originating from a $\text{b}^3\Sigma^+$ state now appears to be incorrect.

The spectra of the N_2O and O_3 flames are so congested and complex that sub-Doppler techniques are required to resolve individual rotational lines. Several years ago, detailed rotational analysis showed that only the $v = 0$ and 1 levels of the $a^3\Pi$ and $A'^1\Pi$ states were responsible for the 600nm bands of the N_2O flame. Largely because only one other low-lying electronic state exists for CaO, we predicted that the carrier of the O_3 flame bands would be the not yet observed $b^3\Sigma^+$ state. On the basis of sub-Doppler excitation and resolved fluorescence spectra of the Ca+ O_3 flame, we now suspect that the O_3 flame bands arise from a single excited vibrational level of the $a^3\Pi$ state.

We expect to complete the analysis of the Ca+ O_3 flame bands (probably $c^3\Sigma^+ + a^3\Pi$) and to search for an explanation of the unusual vibrational and electronic selectivity of the N_2O and O_3 calcium oxidation reactions.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
by	
Distribution/	
Availability Codes	
Dist	Avail and/or
A	Special



II. Publications (since 1 October 1981).

1. S. Churassy et al., "Rotation-Vibration and Deperturbation Analysis of the $\text{BO}_u^+-\text{al}_g$ and $\text{BO}_u^+-\text{a}'\text{O}_g^+$ Systems of I_2 ", J. Chem. Phys. 75, 4863-4868 (1981).
2. R.W. Field, "Tunable Laser Spectroscopy", Faraday Disc. Roy. Soc. Chem. 71, 111-123 (1981).
3. D. Cerny et al., "Nitrogen $\text{B}^3\Pi_g-\text{W}^3\Delta_u$ Laser Systems. Assignment and Model for Observed Lasing Lines," J. Phys. Chem. 85, 2626-2631 (1981).
4. C. Kittrell et al., "Selective Vibrational Excitation by Stimulated Emission Pumping," J. Chem. Phys. 75, 2056-2059 (1981).
5. H.S. Schweda et al., "Highly Excited, Normally Inaccessible Vibrational Levels by Sub-Doppler Modulated Gain Spectroscopy: The $\text{Na}_2 \text{A}^1\Sigma_u^+$ State," Optics Commun. 42, 165-170 (1982).
6. R.F. Marks et al., "The Orange Arc Bands of CaO. Analysis of a $\text{D}, \text{d}^1,3\Delta-\text{a}^3\Pi$ System, J. Chem. Phys. 76, 4689-4691 (1982).
7. R.F. Marks et al., "The CaO $\text{D}, \text{d}^1,3\Delta-\text{a}^3\Pi$ System: Sub-Doppler Spectrum, Rotational Analysis, and Deperturbation", Physica Scripta 25, 312-328 (1982).
8. D. Reisner et al., "Selective Vibrational Excitation of Formaldehyde X^1A_1 by Stimulated Emission Pumping", J. Chem. Phys. 77, 573-575 (1982).
9. E. Abramson et al., "Laser Population of Highly Excited Vibrational Levels of Molecules", Proceedings, Conference on Lasers as Reactants and Probes in Chemistry, 1982.
10. P.H. Vaccaro et al., "Electric Dipole Moments of Excited Vibrational Levels in the X^1A_1 State of Formaldehyde by Stimulated Emission Spectroscopy," J. Chem. Phys. 00, 0000-0000 (1983).

III. Personnel

Co-Principal Investigators:

Robert W. Field
James L. Kinsey

Postdoctorals:

Keith Cross (CaO)
Hai-Lung Dai (H₂CO)
Carter Kittrell (SEP)
Hartmut Schweda (CaO, Na₂)

Graduate Students:

Gunjit Chawla (Na₂)
Caba Korpa (Coriolis)
Jeffrey Norman (CaO)
David Reisner (H₂CO)
Patrick Vaccaro (H₂CO)

Undergraduate Students:

Martin Carerra (H₂CO)
Everett McKay (electronics)

Visiting Scientists:

Roger Bacis (Lyon University; I₂)
Richard Barrow (Oxford; CaO)
Serge Churassy (Lyon University;
Na₂)
Daniel Katayama (Air Force Geo-
physics Lab; SEP)
Li Li (Qinghai Institute, China
Na₂)